Specificity of ion–water interactions is reflected in the way such properties as the partial molar entropies, heat capacities and compressibilities of ions in aqueous solutions depend on ionic radii. Also, ion specificity arises in such spectroscopic properties as the ^1H nmr chemical shift and the changes in overtone stretching and bending infrared band frequencies in water caused by the presence of ions. These properties, derived for individual ions, will be examined in relation to specificity of adsorption of ions at electrodes, especially Hg and Pt.

At the former metal, hydration effects in ion adsorption can be investigated in studies of the adsorption of alkylammonium ions in the series $R_n\overset{+}{N}H_{4-n}$ where $1 \leqslant n \leqslant 4$. Here the hydration of the N^+ centre is controlled by steric effects associated with varying coordination of the N-atom by R groups (R = Me or Et). When n = 4, at the tetraalkylammonium type of ion, hydrophobic adsorption effects arise and the unusual dependence of standard free entropy of adsorption of the cation on coverage can be accounted for in terms of hydration co-sphere sharing effects in the two-dimensional interphase at the Hg electrode. $\Delta H/\Delta S$ compensation effects in adsorption at Hg from aqueous medium indicate the importance of water structure effects in the interphase.

Generally, it is found that the dependence of thermodynamic and spectroscopic properties on ionic size or charge density for cations is quite different from that for anions. This effect is connected with the different orientation of OH bonds and lone-pair electrons in water molecules at anions in comparison with cations. At the former, better H-bonding in hydration shells with the remainder of the solvent can arise for reasons connected with H_2O dipole orientation.

In the case of Pt, interesting information on the state of adsorbed ions such as Cl^-, Br^-, I^-, $CF_3SO_3^-$ and PF_6^- can be derived from their competitive adsorption behaviour *vis à vis* chemisorbed H and OH or O species. In particular, information on lateral interactions and the electrosorption valence can be derived.

Role of Specifically Adsorbed Electrochemically Inert Species in the Electrode Kinetics

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The problem of decoding the physico-chemical mechanism of interaction between the elementary act of an electrochemical reaction and the adsorption phenomena at a metal–solution interface is of major importance because it directly concerns the interpretation of electrochemical kinetics data and the proper mathematical description of the effect of the electric double layer on electrode processes. In connection with the latter aspect the fundamental problem arises, namely, the problem of adequate statistico-mechanical approaching the transition from the description of the elementary act of an electrochemical process occurring at the interface in the presence of electroinactive specifically adsorbed species, ions or dipole molecules, to the description of the resulting heterogeneous process the rate of which is experimentally measurable. The advances made in recent years in interpretation of the data on the kinetics of electrode processes involving the specific adsorption of ionic and dipole solution components relate mainly to substantiation of the role of the discreteness effects. The local electric field acting near the interface on discrete particles possessing electric charge or dipole moment differs, due to polarization of the interface by these particles, from the average field described by the macroscopic equations of electrodynamics with a continuous charge and dipole moment distribution. The characteristic relaxation times of 'the electrostatic image' forces, *i.e.* the redistribution times of free and bound charges at the interface due to its polarization by discrete particles present in solution, are of the order to 10^{-15}–10^{-14} sec. The characteristic times of many types of electrochemical reactions, however, are comparable with the fluctuation reorientation time of dipole molecules of the solvent in the solvation shells of reactants ($\sim 10^{-11}$ sec), *i.e.* they are by three–four orders of magnitude higher than the relaxation times of 'the electrostatic self-image' forces. For this reason, the discrete nature of charges and dipole moments should affect the probability of the elementary act of an electrochemical process. Moreover, the local electric field associated with the discreteness effect can influence the rate of electrochemical processes by changing the concentration of reactants and reaction products inside the layer adjacent to the electrode.

In the present paper the problem of statistico-mechanical averaging the probability of the elementary act of an irreversible electron transfer reaction occurring on a metal–solution interface in the presence of specifically adsorbed electrochemically inert ions or dipole molecules is discussed in detail. The analytical expressions are derived for the polarization curve of the interface in cases of localization of the reactants both inside and outside the compact part of the electric double layer. Within the framework of the theory presented the available experimental data on electrochemical kinetics complicated by the specific adsorption of charged and neutral components of the solution are analysed.

Statistical Mechanical Theories of the Electric Double Layer

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A comparison is made of different recent developments in theories of the electric double layer in aqueous media, based on statistical mechanics. An important advance was made when Henderson, Blum and co-workers showed how the Ornstein–Zernike equations, which originally applied to bulk liquid mixtures, could be modified to yield the density and charge distributions in the diffuse layer next to a charged wall. The interface solution system was treated as a mixture in which the wall of the interface is a solute particle which is exceedingly large in size but small in concentration. In the case of electrolytes (systems with Coulombic forces) a correction was necessary to earlier formulations of the theory. Various approximations well-known in modern statistical mechanical theories of liquids were used by the above authors in the Ornstein–Zernike equations modified to apply at a plane interface. All these approximations make use of the primitive model of an electrolyte, in which ions are treated as charged hard spheres embedded in a continuous solvent medium with a uniform dielectric permittivity so that the ions (and their hydration shells) have the same permittivity as the bulk electrolyte. The hypernetted chain (HNC) approximation, which has been very successful for bulk electrolytes was shown to be equivalent to the non-linear Poisson–Boltzmann (P.B.) equation of Gouy and Chapman, when the effects of the ionic hard-sphere terms can be ignored. Another approach, the so-called mean spherical approximation (MSA), corresponds to the Gouy–Chapman–Stern (GCS) theory at small potentials (linearised P.B. or Debye–Huckel equation). In the GCS theory, the ions interact with the interfacial wall as hard-spheres but continue to interact with each other as point charges. In the MSA ion-size effects are taken into account in a consistent manner. Although the differential capacity of the charged interface is calculated by the MSA theory and compared with that derived from the Stern theory, there is an important difference. The inner region capacity is much too large in the MSA theory because the effective dielectric permittivity of the inner region is put equal to that of bulk electrolyte.

Monte Carlo calculations of the electric double layer, based on statistical mechanics, have been performed by Torrie and Valleau, who use the primitive model of the bulk electrolyte. Their concentration profiles in the diffuse layer are in good agreement even up to 1 *M* with the so-called modified Gouy–Chapman (MGC) theory, which introduces an inner region with the same permittivity as the bulk electrolyte. However the criticism mentioned above about the use of bulk permittivity applies also to these calculations.

An entirely different approach to electric double layer theory has been used by the authors and co-workers. This develops a modified Poisson–Boltzmann (MPB) equation for the electrostatic potential in the diffuse layer, which is based on the classical work of Kirkwood in strong electrolyte theory. The exclusion volume term and the fluctuation term are re-introduced, again with a primitive model of the bulk electrolyte. Making use of a ‘closure’ procedure originally due to Loeb for handling the fluctuation terms, the classical P.B. equation is replaced by a non-linear differential-difference equation which is solved numerically. At moderate electrolyte concentrations (>1 *M*) the mean electrostatic potential and the distribution of ions in the diffuse layer exhibit a damped oscillatory behaviour. The MSA shows similar oscillations which are attributed to ion-size effects, neglected in the P.B. equation. Physically the damped oscillatory behaviour means that there is a stratification of charge in the vicinity of the interface which depends primarily on the electrolyte concentration. At low surface charge and electrolyte concentration, the exclusion volume term has negligible effect compared to the fluctuation term but as the surface charge or electrolyte concentration is increased, the exclusion volume term becomes increasingly important. Comparison of the differential capacitance is made with preliminary calculations of Henderson, Blum and Smith, based on the HNC and identical behaviour is obtained at low surface charge. In both theories, the permittivity of the Stern inner region is equated to the bulk permittivity. Effects relating to solvent structure still remain to be incorporated. Solvent effects have been considered by Ninham and his school, using the Percus–Yevick and HNC equations, but these have been confined to non-coulombic solutes. Improvements in the model of the Stern layer can be incorporated into our theory based on the MPB equation. Also by adapting related work in the electrolyte bulk by one of the authors (C.W.) it is possible that some solvent effects can be incorporated into the MPB equation.